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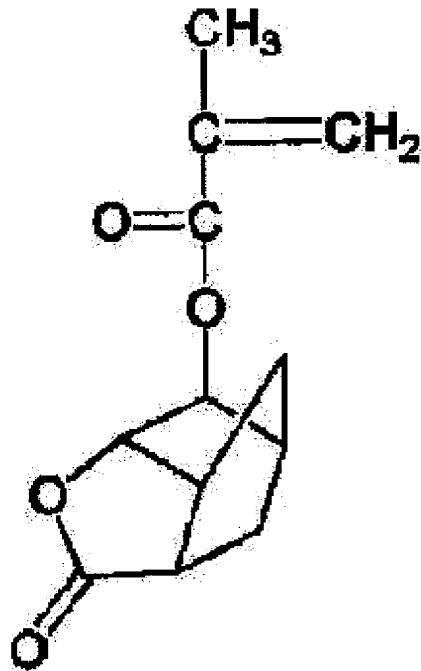
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(54) RADIATION-SENSITIVE RESIN COMPOSITION



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a radiation-sensitive resin composition having high transparency to a radiation and useful as a chemically amplified resist excellent in sensitivity, resolution, dry etching resistance and pattern shape.

SOLUTION: The radiation-sensitive resin composition comprises (A) a resin typified by a copolymer of 2-methyl-2-adamantyl methacrylate, 3-hydroxy-1-adamantyl methacrylate and a methacrylic ester of formula (1), (B) a radiation-sensitive acid generator typified by triphenylsulfonium nonafluoro-n-butanesulfonate or 1-(4-n-butoxy-1-naphthyl)tetrahydrothiophenium perfluoro-n-octanesulfonate and (C) a solvent. Preferably the solvent (C) includes at least one selected from the group comprising propylene glycol monomethyl ether acetate, 2-heptanone and cyclohexanone.

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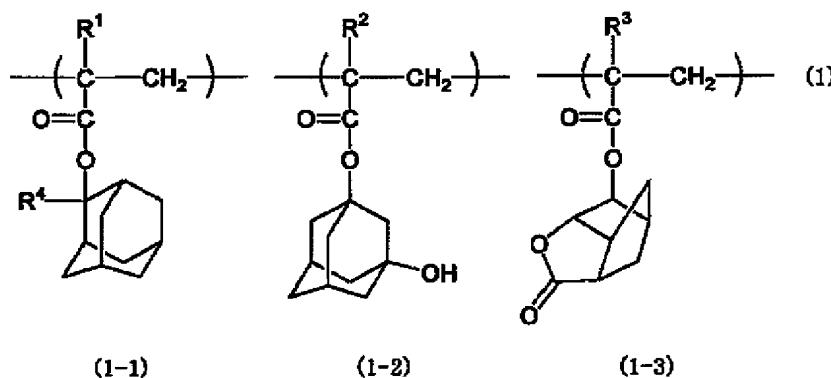
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CLAIMS

[Claim(s)]

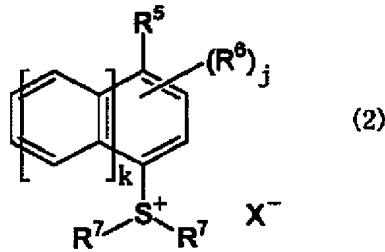
[Claim 1] (A) Contain the repeat unit (1-1), repeat unit (1-2), and repeat unit (1-3) which are shown in the following general formula (1) as an indispensable unit. It is alkali insoluble or alkali poorly soluble resin which serves as alkali fusibility according to an operation of an acid. The content of a repeat unit (1-1) is in 35-50-mol the range in which it is %. And the resin which has the content of a repeat unit (1-2) in 5-30-mol the range in which it is %, the radiation-sensitive acid generator containing the compound expressed with the (B) following general formula (2), the radiation-sensitive resin constituent characterized by containing the (C) solvent in a list.

〔Formula 1〕



In [general formula (1), R1, R2, and R3 show a hydrogen atom or a methyl group independently of mutual, and R4 shows the alkyl group of the shape of a straight chain of carbon numbers 1–6, and the letter of branching.]

[Formula 2]



In [general formula (2) R5 The alkyl group of a hydrogen atom, a hydroxyl group, the shape of a straight chain of carbon numbers 1–10, and the letter of branching, The alkoxy carbonyl group of the alkoxy group of the shape of a straight chain of carbon numbers 1–10 and the letter of branching, the shape of a straight chain of carbon numbers 2–11, and the letter of branching is shown. R6 The alkyl group of a hydrogen atom or the shape of a straight chain of carbon numbers 1–10, and the letter of branching is shown. j — the integer of 0–3 — being shown — every — R7 mutual — independent — the alkyl group of the shape of a straight chain of carbon numbers 1–10, and the letter of branching — [whether the phenyl group which may be permuted, or the naphthyl group by which the substituent may be carried out is shown, and] two R7 [or] it joins

together mutually, the divalent radical of carbon numbers 2-10 is formed, and this divalent radical is permuted -- having -- **** -- k -- the integer of 0-2 -- being shown -- X- C_n F_{2n+1}SO₃- The anion which has structure is shown and n shows the integer of 1-10.]

[Claim 2] (C) The radiation-sensitive resin constituent according to claim 1 characterized by including at least one sort as which a solvent is chosen from the group of propylene-glycol-monomethyl-ether acetate, 2-heptanone, and a cyclohexanone.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the radiation-sensitive resin constituent which can be suitably used for micro processing which uses various kinds of radiations like charged-particle lines, such as X-rays, such as far ultraviolet rays represented by a KrF excimer laser or the ArF excimer laser and a synchrotron radiation line, and an electron ray, as a useful chemistry magnification mold resist.

[0002]

[Description of the Prior Art] In the field of micro processing represented by manufacture of an integrated circuit device, in order to obtain a higher degree of integration, recently, the lithography technique in which micro processing with a level of 0.20 micrometers or less is possible is needed. However, in the conventional lithography process, although near ultraviolet rays, such as i line, are generally used as a radiation, by this near ultraviolet ray, micro processing of subquarter micron level is said to be very difficult. Then, in order to make possible micro processing with a level of 0.20 micrometers or less, utilization of a radiation with more short wavelength is considered. Although the bright line spectrum of a mercury-vapor lamp, the far ultraviolet rays represented by the excimer laser, an X-ray, an electron ray, etc. can be mentioned as a radiation of such short wavelength, for example, the KrF excimer laser (wavelength of 248nm) or the ArF excimer laser (wavelength of 193nm) attracts attention especially among these. Many resists (henceforth a "chemistry magnification mold resist") which used the chemistry magnification effectiveness by the component which has an acid dissociation nature functional group, and the component (henceforth an "acid generator") which generates an acid by the exposure (henceforth "exposure") of a radiation as a resist suitable for the exposure by such excimer laser are proposed. As a chemistry magnification mold resist, the resist containing the polymer which has t-butyl ester group of a carboxylic acid or t-butyl carbo NATO radical of a phenol, and an acid generator is proposed by JP,2-27660,B, for example. This resist uses the phenomenon in which t-butyl ester group or t-butyl carbo NATO radical which exists in a polymer dissociates, and come to have the acidic group which this polymer becomes from a carboxyl group or a phenolic hydroxyl group, consequently the exposure field of a resist coat serves as soluble at an alkali developer according to an operation of the acid generated by exposure.

[0003] By the way, although many of conventional chemistry magnification mold resists use phenol system resin as the base If far ultraviolet rays are used as a radiation in the case of such resin, since it will originate in the aromatic series ring in resin and far ultraviolet rays will be absorbed, There is a fault that the exposed

far ultraviolet rays cannot fully reach to the lower layer section of a resist coat. Therefore, there was much light exposure in the management of a resist coat, in the lower layer section, it decreased, and became such thick trapezoidal shape, and there were problems — sufficient resolution is not obtained — that the upper part is thin and the resist pattern after development goes to the lower part. When the resist pattern after development moreover became trapezoidal shape and the following process, i.e., etching, placing of ion, etc., was performed, desired dimensional accuracy could not be attained but it had become a problem. And when the configuration of the resist pattern upper part was not a rectangle, there was also a problem to which the disappearance rate of the resist by dry etching becomes quick, and control of etching conditions becomes difficult. On the other hand, the configuration of a resist pattern can improve by raising the rate of a radioparency of a resist coat. For example, the chemistry magnification mold resist which the acrylate system resin represented by polymethylmethacrylate (meta) has high transparency also to far ultraviolet rays, and is very desirable resin from a viewpoint of the rate of a radioparency, for example, used methacrylate system resin for JP,4-226461,A is proposed. However, although it is excellent in respect of the micro-processing engine performance, since it does not have an aromatic series ring, this constituent has the fault that dry etching resistance is low, it is difficult to perform etching processing of high degree of accuracy also in this case, and it cannot say it as what combines the transparency over a radiation, and dry etching resistance.

[0004] Moreover, the chemistry magnification mold resist which used the acrylate system resin which the approach of replacing with an aromatic series ring and introducing an aliphatic series ring into the resinous principle in a resist about a chemistry magnification mold resist as one of the policies which improve dry etching resistance without spoiling the transparency over a radiation is learned, for example, has an aliphatic series ring in JP,7-234511,A (meta) is proposed. however, in this resist, as an acid dissociation nature functional group which a resinous principle has The radical (for example, acetal system functional groups, such as a tetrahydropyranyl group) which is comparatively easy to dissociate with the conventional acid, and the radical which is comparatively hard to dissociate with an acid (For example, t-butyl system functional groups, such as t-butyl ester group and t-butyl carbonate radical) are used, and, in the case of the resinous principle which has the former acid dissociation nature functional group, the basic physical properties especially the sensibility, and the pattern configuration of a resist are good, but In the resinous principle which a difficulty is in the preservation stability as a constituent, and has the latter acid dissociation nature functional group, although preservation stability is conversely good, there is a fault that the basic physical properties especially the sensibility, and the pattern configuration of a resist are spoiled. Furthermore, since the aliphatic series ring was introduced into the resinous principle in this resist, the hydrophobicity of resin itself became very high and there was a problem also in respect of the adhesive property over a substrate. Moreover, in case a resist pattern is formed using a chemistry magnification mold resist, in order to promote dissociation of an acid dissociation nature functional group, it is usually heat-treated after exposure, but if whenever [stoving temperature] changes, also changing the line breadth of a resist pattern to some extent will not usually be avoided. However, development of a resist with small fluctuation (namely, temperature dependence) of line breadth has also come to be strongly called for also from change of whenever [after exposure / stoving temperature] reflecting detailed-izing of the integrated circuit device in recent years.

[0005] furthermore, in a chemistry magnification mold resist, the quantum yield of acid generating it is known

that an acid generator will have big effect on the function as a resist, and according to exposure at today is high, and it is high sensitivity -- etc. -- the onium salt compound is widely used as an acid generator of a chemistry magnification resist from the reason. As said onium salt compound, although triphenylsulfonium trifluoromethane sulfonate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium naphthalene sulfonate, cyclohexyl methyl (2-oxocyclohexyl) sulfonium trifluoromethane sulfonate, etc. are used, it cannot be said that these conventional onium salt compounds are still enough in respect of the resist engine performance which generally could not be satisfied in respect of sensibility, and synthesized resolution, a pattern configuration, etc. even when sensibility was comparatively high, for example. Under such a situation, it can be adapted for the radiation of the short wavelength represented by far ultraviolet rays from a viewpoint of ED that it can respond to progress of detailed-izing in an integrated circuit device, and the transparency over a radiation is high and the chemistry magnification mold resist excellent in the basic physical properties as resists, such as sensibility, resolution, and a pattern configuration, is called for strongly.

[0006]

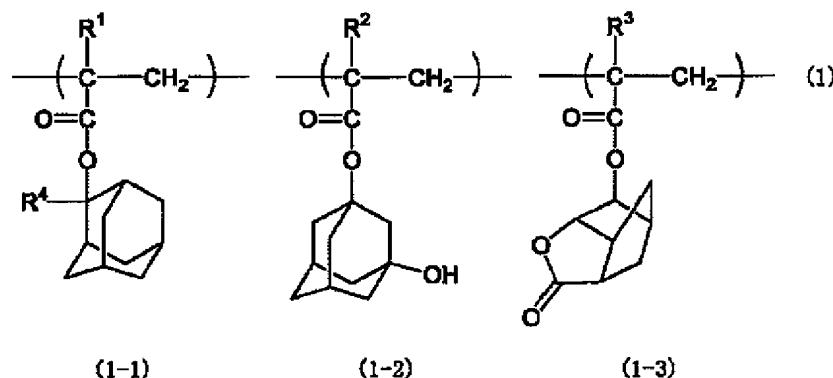
[Problem(s) to be Solved by the Invention] The technical problem of this invention is to offer a radiation-sensitive resin constituent high the transparency over a radiation and useful as a chemistry magnification mold resist which is excellent in sensibility, resolution, dry etching resistance, a pattern configuration, etc.

〔0007〕

[Means for Solving the Problem] The repeat unit which shows said technical problem in the (A) following general formula (1) according to this invention (1-1), A repeat unit (1-2) and a repeat unit (1-3) are contained as an indispensable unit. It is alkali insoluble or alkali poorly soluble resin which serves as alkali fusibility according to an operation of an acid. The content of a repeat unit (1-1) is in 35-50-mol the range in which it is %. And the content of a repeat unit (1-2) is attained by the radiation-sensitive resin constituent characterized by containing the (C) solvent in the resin in 5-30-mol the range which is %, the radiation-sensitive acid generator containing the compound expressed with the (B) following general formula (2), and a list.

[0008]

[Formula 3]

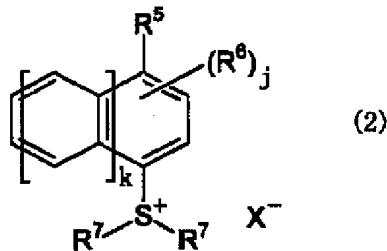


In [general formula (1), R1, R2, and R3 show a hydrogen atom or a methyl group independently of mutual, and

R4 shows the alkyl group of the shape of a straight chain of carbon numbers 1–6, and the letter of branching.]

[0009]

[Formula 4]



In [general formula (2) R5 The alkyl group of a hydrogen atom, a hydroxyl group, the shape of a straight chain of carbon numbers 1–10, and the letter of branching, The alkoxy carbonyl group of the alkoxy group of the shape of a straight chain of carbon numbers 1–10 and the letter of branching, the shape of a straight chain of carbon numbers 2–11, and the letter of branching is shown. R6 The alkyl group of a hydrogen atom or the shape of a straight chain of carbon numbers 1–10, and the letter of branching is shown. j — the integer of 0–3 — being shown — every — R7 mutual — independent — the alkyl group of the shape of a straight chain of carbon numbers 1–10, and the letter of branching — [whether the phenyl group which may be permuted, or the naphthyl group by which the substituent may be carried out is shown, and] two R7 [or] it joins together mutually, the divalent radical of carbon numbers 2–10 is formed, and this divalent radical is permuted — having — **** — k — the integer of 0–2 — being shown — X- Cn F2n+1SO3- The anion which has structure is shown and n shows the integer of 1–10.]

[0010] Hereafter, this invention is explained to a detail.

(A) The repeat unit which shows the (A) component in component this invention in said following general formula (1) (1–1), A repeat unit (1–2) and a repeat unit (1–3) are contained as an indispensable unit. It is alkali insoluble or alkali poorly soluble resin which serves as alkali fusibility according to an operation of an acid. Resin which has the content of a repeat unit (1–1) in 50–35–mol the range in which it is %, and has the content of a repeat unit (1–2) in 5–30–mol the range in which it is % (it is hereafter called "resin (A)".) from — it becomes. When the coat which used resin (A) instead of the resist coat concerned is developed under the alkali development conditions adopted in case a resist pattern is formed from the resist coat formed from the radiation-sensitive resin constituent containing resin (A) with "alkali insolubility here or alkali poor solubility", the property which remains after 50% or more of the initial thickness of the coat concerned developing negatives is meant.

[0011] It sets to a repeating unit (1–1), and is R4. As an alkyl group of the shape of a straight chain of carbon numbers 1–6, and the letter of branching, a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, 2-methylpropyl radical, 1-methylpropyl radical, t-butyl, n-pentyl radical, n-hexyl group, etc. can be mentioned, for example. A methyl group, an ethyl group, etc. are desirable among these alkyl groups. In resin (A), a repeating unit (1–1), a repeating unit (1–2), and a repeating unit (1–3) can be independent respectively, or can exist two or more sorts. Repeating unit (1–1) – (1–3) is a repeating unit originating in the acrylic ester (meta) which corresponds, respectively.

[0012] resin (A) can have one or more sorts of repeating units (the following -- " -- others -- it is called repeating unit".) other than repeating unit (1-1) – (1-3). As a polymerization nature partial saturation monomer which gives other repeating units For example, acrylic-acid (meta) norbornyl, acrylic-acid (meta) isobornyl, Acrylic-acid tricyclo deca nil, acrylic-acid (meta) tetracyclo deca nil, (Meta) Acrylic-acid JISHIKURO pentenyl, acrylic-acid (meta) adamanyl, (Meta) The acrylic ester which has owner pons type hydrocarbon frames, such as acrylic-acid 3-hydroxy adamanyl and acrylic-acid (meta) adamanyl methyl, (meta); (meta) Acrylic-acid carboxy norbornyl, (Meta) (Meta) Carboxyl group content ester which has the owner pons type hydrocarbon frame of unsaturated carboxylic acid, such as acrylic-acid carboxy tricyclo deca nil and acrylic-acid (meta) carboxy tetracyclo deca nil;

[0013] A methyl acrylate, an ethyl acrylate (meta), acrylic-acid (meta) n-propyl, (Meta) Acrylic-acid n-butyl, acrylic-acid (meta) 2-methylpropyl, (Meta) Acrylic-acid 2-hydroxyethyl, 2-hydroxypropyl acrylate (meta), (Meta) Acrylic-acid 3-hydroxypropyl, acrylic-acid (meta) cyclo propyl, (Meta) Acrylic-acid cyclopentyl, acrylic-acid (meta) cyclohexyl, (Meta) Acrylic-acid 4-methoxy cyclohexyl, acrylic-acid (meta) 2-cyclopentyloxy carbonylethyl, (Meta) (Meta) Acrylic ester (meta) without owner pons type hydrocarbon frames, such as acrylic-acid 2-cyclohexyloxy carbonylethyl and acrylic-acid (meta) 2-(4-methoxy cyclohexyl) oxy-carbonylethyl;

[0014] alpha-hydroxy methylacrylic acid methyl, alpha-hydroxy methylacrylic acid ethyl, alpha-hydroxy methylacrylic acid ester, such as alpha-hydroxy methylacrylic acid n-propyl and alpha-hydroxy methylacrylic acid n-butyl; (meta) Acrylonitrile, alpha-chloro acrylonitrile, croton nitril, mallein nitril, Unsaturated nitrile compounds, such as fumaronitrile, mesa KONNITORIRU, SHITORAKONNITORIRU, and ITAKON nitril; (meta) Acrylamide, N and N-dimethyl (meta) acrylamide, a croton amide, a mallein amide, Partial saturation amide compounds, such as a fumaric amide, mesa KONAMIDO, SHITORAKONAMIDO, and an ITAKON amide; (meta) Acrylic-acid 2-carboxy ethyl, Acrylic-acid 2-carboxy propyl, acrylic-acid (meta) 3-carboxy propyl, (Meta) (Meta) Monofunctional nature monomers, such as carboxyl group content ester without the owner pons type hydrocarbon frame of unsaturated carboxylic acid, such as acrylic-acid 4-carboxy butyl and acrylic-acid (meta) 4-carboxy cyclohexyl, and [0015] Polyfunctional monomer which has owner pons type hydrocarbon frames, such as 1, 2-adamantane JIORUJI (meta) acrylate, 1, 3-adamantane JIORUJI (meta) acrylate, 1, 4-adamantane JIORUJI (meta) acrylate, and tricyclo deca nil JIMECHIRORUJI (meta) acrylate;

[0016] Methylene GURIKORUJI (meta) acrylate, ethylene GURIKORUJI (meta) acrylate, Propylene GURIKORUJI (meta) acrylate, 1, 6-hexane JIORUJI (meta) acrylate, 2, the 5-dimethyl -2, 5-hexane JIORUJI (meta) acrylate, 1, 8-octane JIORUJI (meta) acrylate, 1, 9-nonane JIORUJI (meta) acrylate, Polyfunctional monomers, such as a polyfunctional monomer without owner pons type hydrocarbon frames, such as 1, 4-bis(2-hydroxypropyl) BENZENJI (meta) acrylate, 1, and 3-bis(2-hydroxypropyl) BENZENJI (meta) acrylate, can be mentioned.

[0017] resin (A) -- setting -- the content of a repeating unit (1-1) -- all repeating units -- receiving -- 35 – 50-mol % -- desirable -- 35 – 45-mol % -- it is 40 – 45-mol % still more preferably. In this case, when the contrast of the exposure section and an unexposed part becomes low, there is an inclination for the resolution as a resist to fall, less than [35 mol %] and the content of a repeating unit (1-1) exceeds 50-mol % on the other hand, exposure allowances become small and there is an inclination for resolution to

fall. moreover, the content of a repeating unit (1-2) -- all repeating units -- receiving -- 5-30-mol % -- desirable -- 5-25-mol % -- it is 10-25-mol % still more preferably. In this case, when an adhesive property with the substrate of a resist pattern falls, there is an inclination for exfoliation of a resist pattern to become easy to take place, less than [5 mol %] and the content of a repeating unit (1-2) exceeds 30-mol % on the other hand, there is an inclination for the resolution as a resist to fall. moreover, the content of a repeating unit (1-3) -- all repeating units -- receiving -- usually -- 20-60-mol % -- desirable -- 25-50-mol % -- it is 30-50-mol % still more preferably. In this case, less than [20 mol %], when solubility [as opposed to the alkali developer of the exposure section in the content of a repeating unit (1-3)] becomes low, there is a possibility of producing Society for Cutting Up Men and 60-mol % is exceeded on the other hand, there is an inclination for the solubility over the solvent of resin to fall. furthermore, the content of other repeating units -- all repeating units -- receiving -- usually -- less than [30 mol %] -- it is less than [20 mol %] preferably. [0018] Radical polymerization initiators, such as hydroperoxide, dialkyl peroxide, diacyl peroxide, and an azo compound, can be used for resin (A) for the polymerization nature partial saturation monomer corresponding to each of that repeating unit, and it can manufacture them by carrying out a polymerization under existence of a chain transfer agent and in a suitable solvent if needed, for example. As a solvent used for said polymerization, for example N pentane, n-hexane, Alkanes, such as n-heptane, n-octane, n-nonane, and n-Deccan; A cyclohexane, Cycloalkanes, such as cycloheptane, cyclooctane, a decalin, and norbornane; Benzene, Aromatic hydrocarbon, such as toluene, a xylene, ethylbenzene, and a cumene; Chloro butane Hexamethylene jib ROMIDO BUROMO hexanes and dichloroethanes -- Halogenated hydrocarbon, such as a chlorobenzene; Ethyl acetate, n-butyl acetate, Ketones, such as saturation carboxylate; 2-butanone, such as acetic-acid i-butyl and methyl propionate, 4-methyl-2-pentanone, and 2-heptanone; EERU, such as a tetrahydrofuran, dimethoxyethane, and diethoxy ethane, can be mentioned. These solvents are independent, or two or more sorts can be mixed and used for them. Moreover, 40-120 degrees C of reaction temperature in said polymerization are usually 50-90 degrees C preferably, and reaction time is usually 1 - 24 hours preferably for 1 to 48 hours.

[0019] the polystyrene equivalent weight average molecular weight (henceforth "Mw") by the gel permeation chromatography (GPC) of resin (A) -- usually -- 3,000-30,000 -- desirable -- 5,000-30,000 -- it is 5,000-20,000 still more preferably. In this case, when there is an inclination for thermal resistance when Mw of resin (A) considers as a resist less than by 3,000 to fall and 30,000 is exceeded on the other hand, there is an inclination for the development nature when considering as a resist to fall. moreover, the ratio (Mw/Mn) of Mw of resin (A), and the polystyrene conversion number average molecular weight (henceforth "Mn") by gel permeation chromatography (GPC) -- usually -- 1-5 -- it is 1-3 preferably. In addition, resin (A) is so desirable that there are few impurities, such as a halogen and a metal, and, thereby, the sensibility when considering as a resist, resolution, process stability, a pattern configuration, etc. can be improved further. As a purification method of resin (A), the combination of chemical purification methods, such as rinsing and a *** extract, these chemical purification methods, and physical purification methods, such as ultrafiltration and centrifugal separation, etc. can be mentioned, for example. In this invention, resin (A) is independent, or two or more sorts can be mixed and used for it.

[0020] (B) The (B) component in component this invention consists of a radiation-sensitive acid generator (henceforth "an acid generator (B)") containing the compound (henceforth "an acid generator (2)")

expressed with said general formula (2). The acid dissociation nature machine which exists in resin (A) is made to dissociate according to an operation of the acid generated by exposure, as a result, the exposure section of a resist coat serves as soluble at an alkali developer, and an acid generator (B) has the operation which forms the resist pattern of a positive type.

[0021] It sets to a general formula (2) and is R5 and R6. As an alkyl group of the shape of a straight chain of carbon numbers 1-10, and the letter of branching For example, a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, 2-methylpropyl radical, 1-methylpropyl radical, t-butyl, n-pentyl radical, a neopentyl radical, n-hexyl group, n-heptyl radical, n-octyl radical, a 2-ethylhexyl radical, n-nonyl radical, n-decyl group, etc. can be mentioned. A methyl group, an ethyl group, n-propyl group, n-butyl, t-butyl, etc. are desirable among these alkyl groups.

[0022] Moreover, R5 As an alkoxy group of the shape of a straight chain of carbon numbers 1-10, and the letter of branching For example, a methoxy group, an ethoxy radical, n-propoxy group, i-propoxy group, An n-butoxy radical, 2-methyl propoxy group, 1-methyl propoxy group, A t-butoxy radical, an n-pentyloxy radical, a neopentyl oxy-radical, an n-hexyloxy radical, n-heptyloxy radical, n-octyloxy radical, 2-ethylhexyloxy radical, n-nonyloxy radical, an n-decyloxy radical, etc. can be mentioned. A methoxy group, an ethoxy radical, an n-butoxy radical, a t-butoxy radical, etc. are desirable among these alkoxy groups.

[0023] Moreover, R5 As an alkoxy carbonyl group of the shape of a straight chain of carbon numbers 2-11, and the letter of branching For example, a methoxycarbonyl group, an ethoxycarbonyl radical, an n-propoxy carbonyl group, An i-propoxy carbonyl group, n-butoxycarbonyl radical, 2-methyl propoxy carbonyl group, 1-methyl propoxy carbonyl group, a t-butoxycarbonyl group, an n-pentyloxy carbonyl group, A neopentyl oxy-carbonyl group, an n-hexyloxy carbonyl group, n-heptyloxy carbonyl group, n-octyloxy carbonyl group, 2-ethylhexyloxy carbonyl group, n-nonyloxy carbonyl group, an n-decyloxy carbonyl group, etc. can be mentioned. A methoxycarbonyl group, an ethoxycarbonyl radical, a t-butoxycarbonyl group, etc. are desirable among these alkoxy carbonyl groups.

[0024] R5 in a general formula (2) If it carries out, a hydrogen atom, a hydroxyl group, a methoxy group, an ethoxy radical, an n-butoxy radical, etc. are desirable.

[0025] R6 in a general formula (2) If it carries out, a hydrogen atom, a methyl group, t-butyl, etc. are desirable.

[0026] It sets to a general formula (2) and is R7. As a phenyl group which may be permuted For example, a phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 2, 3-dimethylphenyl radical, 2, 4-dimethylphenyl radical, 2, 5-dimethylphenyl radical, 2, 6-dimethylphenyl radical, 3, 4-dimethylphenyl radical, 3, 5-dimethylphenyl radical, The shape of phenyl groups, such as 2, 4, 6-trimethyl phenyl radical, and 4-ethyl phenyl group, or a straight chain of carbon numbers 1-10, The phenyl group permuted by the letter of branching, or the annular alkyl group; these phenyl groups or an alkylation phenyl group The radical permuted by one or more pieces, such as hydroxyl, a carboxyl group, a cyano group, a nitro group, an alkoxy group, an alkoxyalkyl group, an alkoxy carbonyl group, and alkoxy carbonyloxy group, or one or more sorts can be mentioned.

[0027] As said alkoxy group, the shape of a straight chain, a letter of branching, or an annular alkoxy group of the carbon numbers 1-20, such as a methoxy group, an ethoxy radical, n-propoxy group, i-propoxy group, an n-butoxy radical, 2-methyl propoxy group, 1-methyl propoxy group, a t-butoxy radical, a cyclopentyloxy

radical, and a cyclohexyloxy radical, etc. can be mentioned among the substituents to a phenyl group and an alkylation phenyl group, for example.

[0028] Moreover, as said alkoxyalkyl group, the shape of a straight chain, a letter of branching, or an annular alkoxyalkyl group of the carbon numbers 2-21, such as a methoxymethyl radical, an ethoxy methyl group, 1-methoxy ethyl group, 2-methoxy ethyl group, 1-ethoxyethyl radical, and 2-ethoxyethyl radical, etc. can be mentioned, for example.

[0029] Moreover, as said alkoxy carbonyl group, the shape of a straight chain, a letter of branching, or an annular alkoxy carbonyl group of the carbon numbers 2-21, such as a methoxycarbonyl group, an ethoxycarbonyl radical, an n-propoxy carbonyl group, an i-propoxy carbonyl group, n-butoxycarbonyl radical, 2-methyl propoxy carbonyl group, 1-methyl propoxy carbonyl group, a t-butoxycarbonyl group, a cyclopentyloxy carbonyl group, and cyclohexyloxy carbonyl, etc. can be mentioned, for example.

[0030] Moreover, as said alkoxy carbonyloxy group, the shape of a straight chain, a letter of branching, or annular alkoxy carbonyloxy group of the carbon numbers 2-21, such as a methoxycarbonyloxy radical, an ethoxycarbonyloxy radical, n-propoxycarbonyloxy radical, i-propoxycarbonyloxy radical, n-butoxycarbonyloxy radical, t-butoxycarbonyloxy radical, a cyclopentyloxy carbonyl group, and cyclohexyloxy carbonyl, etc. can be mentioned, for example.

[0031] R7 in a general formula (2) As a phenyl group which may be permuted, a phenyl group, 4-methoxyphenyl radical, etc. are desirable.

[0032] Moreover, R7 As a naphthyl group which may be permuted For example, 1-naphthyl group, a 2-methyl-1-naphthyl group, a 3-methyl-1-naphthyl group, A 4-methyl-1-naphthyl group, a 4-methyl-1-naphthyl group, a 5-methyl-1-naphthyl group, A 6-methyl-1-naphthyl group, a 7-methyl-1-naphthyl group, a 8-methyl-1-naphthyl group, 2, a 3-dimethyl-1-naphthyl group, 2, a 4-dimethyl-1-naphthyl group, 2, a 5-dimethyl-1-naphthyl group, 2, a 6-dimethyl-1-naphthyl group, 2, a 7-dimethyl-1-naphthyl group, 2, a 8-dimethyl-1-naphthyl group, 3, a 4-dimethyl-1-naphthyl group, 3, a 5-dimethyl-1-naphthyl group, 3, a 6-dimethyl-1-naphthyl group, 3, a 7-dimethyl-1-naphthyl group, 3, a 8-dimethyl-1-naphthyl group, 4, a 5-dimethyl-1-naphthyl group, 5, a 8-dimethyl-1-naphthyl group, a 4-ethyl-1-naphthyl group 2-naphthyl group, The shape of naphthyl groups, such as a 1-methyl-2-naphthyl group, a 3-methyl-2-naphthyl group, and a 4-methyl-2-naphthyl group, or a straight chain of carbon numbers 1-10, The naphthyl group permuted by the letter of branching, or the annular alkyl group; these naphthyl groups or an alkylation naphthyl group The radical permuted by one or more pieces, such as hydroxyl, a carboxyl group, a cyano group, a nitro group, an alkoxy group, an alkoxyalkyl group, an alkoxy carbonyl group, and alkoxy carbonyloxy group, or one or more sorts can be mentioned.

[0033] As the alkoxy group which is a substituent to a naphthyl group and an alkylation naphthyl group, an alkoxyalkyl group, an alkoxy carbonyl group, and alkoxy carbonyloxy group, the same thing as the radical which was illustrated about said phenyl group and the alkylation phenyl group and which corresponds, respectively can be mentioned, for example. R7 in a general formula (2) As a naphthyl group which may be permuted, 1-naphthyl group, a 4-methoxy-1-naphthyl group, etc. are desirable.

[0034] Moreover, two R7 As a divalent radical of the carbon numbers 2-10 which combined mutually and were formed, the cyclic structure of 5 members or 6 members and the radical which forms the cyclic structure (namely, tetrahydrothiophene ring structure) of 5 members preferably especially are desirable in

the sulfur atom in a formula. Moreover, as a substituent to said divalent radical, the hydroxyl illustrated as a substituent to said phenyl group and an alkylation phenyl group, a carboxyl group, a cyano group, a nitro group, an alkoxy group, an ARUKOKI alkyl group, an alkoxy carbonyl group, alkoxy carbonyloxy group, etc. can be mentioned, for example.

[0035] R7 in a general formula (2) ***** -- a methyl group, an ethyl group, t-butyl, a phenyl group, and two R7 The divalent radical which joins together mutually and forms a tetrahydrothiophene ring structure with a sulfur atom is desirable.

[0036] It sets to a general formula (2) and is X. - C_n F_{2n+1}SO₃ - Although an inner C_n F_{2n+1}-radical is a perfluoroalkyl radical of a carbon number n, these radicals can be the shape of a straight chain, and a letter of branching. X - As n which can be set, 4 or 8 are desirable.

[0037] As an example of an acid generator (2), triphenylsulfonium trifluoromethane sulfonate, Triphenylsulfonium nona fluoro-n-butane sulfonate, Triphenylsulfonium perfluoro-n-octane sulfonate, 1-NAFUCHIRUJIMECHIRU sulfonium trifluoromethane sulfonate, 1-naphthyl dimethyl sulfonium NONAFURUORO-n-butane sulfonate, 1-naphthyl dimethyl sulfonium perfluoro-n-octane sulfonate, 1-NAFUCHIRUJIECHIRU sulfonium trifluoromethane sulfonate, 1-naphthyl diethyl sulfonium NONAFURUORO-n-butane sulfonate, 1-naphthyl diethyl sulfonium perfluoro-n-octane sulfonate, [0038] 1-(4-hydroxy naphthyl) dimethyl sulfonium trifluoromethane sulfonate, 1-(4-hydroxy naphthyl) dimethyl sulfonium nona fluoro-n-butane sulfonate, 1-(4-hydroxy naphthyl) dimethyl sulfonium perfluoro-n-octane sulfonate, 1-(4-hydroxy naphthyl) diethyl sulfonium trifluoromethane sulfonate, 1-(4-hydroxy naphthyl) diethyl sulfonium nona fluoro-n-butane sulfonate, 1-(4-hydroxy naphthyl) diethyl sulfonium perfluoro-n-octane sulfonate, 1-(4-methyl naphthyl) dimethyl sulfonium trifluoromethane sulfonate, 1-(4-methyl naphthyl) dimethyl sulfonium nona fluoro-n-butane sulfonate, 1-(4-methyl naphthyl) dimethyl sulfonium perfluoro-n-octane sulfonate, 1-(4-methyl naphthyl) diethyl sulfonium trifluoromethane sulfonate, 1-(4-methyl naphthyl) diethyl sulfonium nona fluoro-n-butane sulfonate, 1-(4-methyl naphthyl) diethyl sulfonium perfluoro-n-octane sulfonate, [0039] 1-(4-cyano naphthyl) dimethyl sulfonium trifluoromethane sulfonate, 1-(4-cyano naphthyl) dimethyl sulfonium nona fluoro-n-butane sulfonate, 1-(4-cyano naphthyl) dimethyl sulfonium perfluoro-n-octane sulfonate, 1-(4-cyano naphthyl) diethyl sulfonium trifluoromethane sulfonate, 1-(4-cyano naphthyl) diethyl sulfonium nona fluoro-n-butane sulfonate, 1-(4-cyano naphthyl) diethyl sulfonium perfluoro-n-octane sulfonate, 1-(4-nitro naphthyl) dimethyl sulfonium trifluoromethane sulfonate, 1-(4-nitro naphthyl) dimethyl sulfonium nona fluoro-n-butane sulfonate, 1-(4-nitro naphthyl) dimethyl sulfonium perfluoro-n-octane sulfonate, 1-(4-nitro naphthyl) diethyl sulfonium trifluoromethane sulfonate, 1-(4-nitro naphthyl) diethyl sulfonium nona fluoro-n-butane sulfonate, 1-(4-nitro naphthyl) diethyl sulfonium perfluoro-n-octane sulfonate, [0040] 1-(3, 5-dimethyl-4-hydroxyphenyl) tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 1-(3, 5-dimethyl-4-hydroxyphenyl) tetrahydro thio FENIUMUNONA fluoro-n-butane sulfonate, 1-(3, 5-dimethyl-4-hydroxyphenyl) tetrahydro thio FENIUMUNONA perfluoro-n-octane sulfonate, 1-(4-methoxy naphthalene-1-IRU) tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 1-(4-methoxy naphthalene-1-IRU) tetrahydro thio FENIUMUNONA fluoro-n-butane sulfonate, 1-(4-methoxy naphthalene-1-IRU) tetrahydro thio FENIUMUNONA perfluoro-n-octane sulfonate, 1-(4-ethoxy naphthalene-1-IRU) tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 1-(4-ethoxy naphthalene-1-IRU) tetrahydro thio FENIUMUNONA fluoro-n-butane sulfonate,

1-(4-ethoxy naphthalene-1-IRU) tetrahydro thio FENIUMU perfluoro-n-octane sulfonate, 1-(4-n-butoxy naphthalene-1-IRU) tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 1-(4-n-butoxy naphthalene-1-IRU) tetrahydro thio FENIUMUNONA fluoro-n-butane sulfonate, 1-(4-n-butoxy naphthalene-1-IRU) tetrahydro thio FENIUMU perfluoro-n-octane sulfonate, etc. can be mentioned.

[0041] The triphenylsulfonium nona fluoro-n-butane sulfonate among these acid generators (2), Triphenylsulfonium perfluoro-n-octane sulfonate, 1-(3, 5-dimethyl-4-hydroxyphenyl) tetrahydro thio FENIUMUNONA fluoro-n-butane sulfonate, 1-(3, 5-dimethyl-4-hydroxyphenyl) tetrahydro thio FENIUMU perfluoro-n-octane sulfonate, 1-(4-n-butoxy naphthalene-1-IRU) tetrahydro thio FENIUMUNONA fluoro-n-butane sulfonate, 1-(4-n-butoxy naphthalene-1-IRU) tetrahydro thio FENIUMU perfluoro-n-octane sulfonate, etc. are desirable. In this invention, an acid generator (2) is independent, or two or more sorts can be mixed and used for it.

[0042] moreover, in this invention, other radiation-sensitive acid generators (the following — “— others — it is called acid generator”.) can be used together with an acid generator (2). As other acid generators, an onium salt compound, a halogen content compound, a diazoketone compound, a sulfone compound, a sulfonic-acid compound, etc. can be mentioned, for example. The following can be mentioned as other acid generators of these.

[0043] Onium-salt compound: As an onium salt compound, iodonium salt, sulfonium salt, phosphonium salt, diazonium salt, pyridinium salt, etc. can be mentioned, for example. As an example of an onium salt compound, diphenyliodonium trifluoromethane sulfonate, Diphenyliodonium nona fluoro-n-butane sulfonate, diphenyliodonium perfluoro-n-octane sulfonate, Bis(4-t-butylphenyl) iodonium trifluoromethane sulfonate, Bis(4-t-butylphenyl) iodonium nona fluoro-n-butane sulfonate, Bis(4-t-butylphenyl) iodonium perfluoro-n-octane sulfonate, Cyclohexyl and 2-oxocyclohexyl methyl sulfonium trifluoromethane sulfonate, Dicyclohexyl and 2-oxocyclohexyl sulfonium trifluoromethane sulfonate, 2-oxocyclohexyl dimethyl sulfonium trifluoromethane sulfonate, etc. can be mentioned.

[0044] Halogen content compound: As a halogen content compound, a halo alkyl group content hydrocarbon compound, a halo alkyl group content heterocyclic compound, etc. can be mentioned, for example. As an example of a halogen content compound, they are (TORIKURORO methyl)-s-triazine derivatives, such as phenyl bis(TORIKURORO methyl)-s-triazine, 4-methoxyphenyl bis(TORIKURORO methyl)-s-triazine, and 1-naphthyl bis(TORIKURORO methyl)-s-triazine, and 1 and 1-screw (4-chlorophenyl). - 2, 2, and 2-trichloroethane etc. can be mentioned.

Diazoketone compound: As a diazoketone compound, 1, a 3-diketo-2-diazo compound, a diazo benzoquinone compound, a diazo naphthoquinone compound, etc. can be mentioned, for example. As an example of diazoketone, 1, 2-naphthoquinonediazide-4-sulfonyl chloride, A 1 of 1, 2-naphthoquinonediazide-5-sulfonyl chloride, 2, 3 and 4, and 4'-tetra-hydroxy benzophenone, and 2-naphthoquinonediazide-4-sulfonate or 1, a 2-naphthoquinonediazide-5-sulfonate, A 1, 1, 1 of 1-tris (4-hydroxyphenyl) ethane, and 2-naphthoquinonediazide-4-sulfonate or 1, and 2-naphthoquinonediazide-5-sulfonate etc. can be mentioned.

[0045] Sulfone compound: As a sulfone compound, a beta-keto sulfone, beta-sulfonyl sulfone, alpha-diazo compound of these compounds, etc. can be mentioned, for example. As an example of a sulfone compound, 4-tris phenacyl sulfone, a mesityl phenacyl sulfone, bis(phenyl sulfonyl) methane, etc. can be mentioned.

Sulfonic-acid compound: As a sulfonic-acid compound, an alkyl sulfonate, alkyl sulfonic-acid imide, a halo alkyl sulfonate, an aryl sulfonate, imino sulfonate, etc. can be mentioned, for example. As an example of a sulfonic-acid compound, benzoin tosylate, the tris of pyrogallol (trifluoromethane sulfonate), Nitrobenzyl-9, 10-diethoxy anthracene-2-sulfonate, The trifluoromethane sulfonyl bicyclo [2.2.1] hept-5-en-2, 3-JIKARUBO diimide, The nona fluoro-n-butane sulfonyl bicyclo [2.2.1] hept-5-en-2, 3-JIKARUBO diimide, The perfluoro-n-octane sulfonyl bicyclo [2.2.1] hept-5-en-2, 3-JIKARUBO diimide, N-hydroxy SUKUSHIIMIDO trifluoromethane sulfonate, N-hydroxy SUKUSHIIMIDO nona fluoro-n-butane sulfonate, N-hydroxy SUKUSHI imide perfluoro-n-octane sulfonate, 1, 8-naphthalene dicarboxylic acid imide trifluoromethane sulfonate, 1, 8-naphthalene dicarboxylic acid imide nona fluoro-n-butane sulfonate, 1, and 8-naphthalene dicarboxylic acid imide perfluoro-n-octane sulfonate etc. can be mentioned.

[0046] The diphenyliodonium trifluoromethane sulfonate among other acid generators of these, Diphenyliodonium nona fluoro-n-butane sulfonate, diphenyliodonium perfluoro-n-octane sulfonate, Bis(4-t-buthylphenyl) iodonium trifluoromethane sulfonate, Bis(4-t-buthylphenyl) iodonium nona fluoro-n-butane sulfonate, Bis(4-t-buthylphenyl) iodonium perfluoro-n-octane sulfonate, Cyclohexyl and 2-oxocyclohexyl methyl sulfonium trifluoromethane sulfonate, Dicyclohexyl and 2-oxocyclohexyl sulfonium trifluoromethane sulfonate, 2-oxocyclohexyl dimethyl sulfonium trifluoromethane sulfonate, [0047] The trifluoromethane sulfonyl bicyclo [2.2.1] hept-5-en-2, 3-JIKARUBO diimide, The nona fluoro-n-butane sulfonyl bicyclo [2.2.1] hept-5-en-2, 3-JIKARUBO diimide, The perfluoro-n-octane sulfonyl bicyclo [2.2.1] hept-5-en-2, 3-JIKARUBO diimide, N-hydroxy SUKUSHIIMIDO trifluoromethane sulfonate, N-hydroxy SUKUSHIIMIDO nona fluoro-n-butane sulfonate, N-hydroxy SUKUSHI imide perfluoro-n-octane sulfonate, 1, and 8-naphthalene dicarboxylic acid imide trifluoromethane sulfonate etc. is desirable. An acid generator besides the above is independent, or two or more sorts can be mixed and used for it.

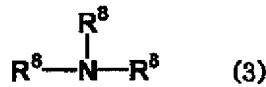
[0048] the (Resin A) 100 weight section from a viewpoint from which the amount of the sum total used of an acid generator (2) and other acid generators secures the sensibility and development nature as a resist in this invention -- receiving -- usually -- 0.1 -- 20 weight section -- it is 0.5 -- 10 weight section preferably. In this case, there is an inclination which becomes [said amount of the sum total used] the transparency over a radiation falling and being able to be hard to obtain a rectangular resist pattern if there is an inclination for sensibility and development nature to fall, under in the 0.1 weight section and 20 weight sections are exceeded on the other hand. Moreover, the operating rate of other acid generators is usually 60 or less % of the weight preferably 80 or less % of the weight to the sum total of an acid generator (2) and other acid generators. In this case, when the operating rate of other acid generators exceeds 80 % of the weight, there is a possibility that the expected effectiveness of this invention may be spoiled.

[0049] Various kinds of additives, such as an acid diffusion control agent, an alicycle group additive which has an acid dissociation nature machine, a surfactant, and a sensitizer, can be blended with the radiation-sensitive resin constituent of additive this invention if needed. Said acid diffusion control agent is a component which has the operation which controls the diffusion phenomenon in the resist coat of the acid produced from an acid generator by exposure, and controls the chemical reaction in a non-exposing field which is not desirable. While the storage stability of the radiation-sensitive resin constituent obtained by blending such an acid diffusion control agent improves and the resolution as a resist improves further, line breadth change of the resist pattern by fluctuation of the length soaking time (PED) from exposure to the

heat-treatment after exposure can be suppressed, and the constituent which was extremely excellent in process stability is obtained. As an acid diffusion control agent, the nitrogen-containing organic compound from which basicity does not change with the exposure or heat-treatment in the formation process of a resist pattern is desirable. As such a nitrogen-containing organic compound, it is the following general formula (3), for example.

[0050]

[Formula 5]



[general formula (3) -- setting -- every -- R8 shows the unsubstituted shape of a hydrogen atom, a permutation, or a straight chain, the letter of branching or an annular alkyl group, a permutation, an unsubstituted aryl group, a permutation, or an unsubstituted aralkyl radical independently of mutual.]

[0051] It can come out and the compound (henceforth "nitrogen-containing compound (**)") expressed, the compound (henceforth "nitrogen-containing compound (**)") which has two nitrogen atoms in the same intramolecular, the Pori amino compound which has three or more nitrogen atoms, a polymer (these are hereafter called collectively "nitrogen-containing compound (Ha)"). and an amide group content compound, an urea compound, a nitrogen-containing heterocyclic compound, etc. can be mentioned.

[0052] As nitrogen-containing compound (b), for example n-hexylamine, n-heptyl amine, Monochrome (cyclo) alkylamines, such as n-octyl amine, n-nonyl amine, n-DESHIRU amine, and cyclohexylamine; G n butylamine, G n-pentylamine, G n-hexylamine, a G n-heptyl amine, A G n-octyl amine, a G n-nonyl amine, a G n-DESHIRU amine, JI (cyclo) alkylamines, such as cyclohexyl monomethylamine and dicyclohexylamine; Triethylamine, Tree n propylamine, tree n butylamine, tree n-pentylamine, Tree n-hexylamine, a tree n-heptyl amine, a tree n-octyl amine, A tree n-nonyl amine, a tree n-DESHIRU amine, cyclohexyl dimethylamine, The Tori (cyclo) alkylamines, such as methyl dicyclohexylamine and tricyclo hexylamine; An aniline, Aromatic amine, such as N-methylaniline, N,N-dimethylaniline, 2-methylaniline, 3-methylaniline, 4-methylaniline, 4-nitroaniline, a diphenylamine, a triphenylamine, and a naphthylamine, can be mentioned.

[0053] As nitrogen-containing compound (b), for example Ethylenediamine, N and N, N', N'-tetramethylethylenediamine, Tetramethylenediamine, hexamethylenediamine, 4, and 4'-diamino diphenylmethane, A - diamino diphenyl ether, and 4 and 4' 4, 4'-diamino benzophenone, A 4 and 4'-diamino diphenylamine, 2, and 2-bis(4-aminophenyl) propane, A 2-(3-aminophenyl)-2-(4-aminophenyl) propane, A 2-(4-aminophenyl)-2-(3-hydroxyphenyl) propane, A 2-(4-aminophenyl)-2-(4-hydroxyphenyl) propane, 1, 4-bis[1-(4-aminophenyl)-1-methylethyl] benzene, 1 and 3-bis[1-(4-aminophenyl)-1-methylethyl] benzene, the bis(2-dimethylaminoethyl) ether, the bis(2-diethylaminoethyl) ether, etc. can be mentioned. As a nitrogen-containing compound (Ha), the polymer of polyethyleneimine, the poly allylamine, and 2-dimethylaminoethyl acrylamide etc. can be mentioned, for example.

[0054] As said amide group content compound, for example A N-t-butoxy cull BONIRUJI-n-octyl amine, A N-t-butoxy cull BONIRUJI-n-nonyl amine, a N-t-butoxy cull BONIRUJI-n-DESHIRU amine, N-t-butoxy cull BONIRUJI cyclohexylamine, an N-t-butoxycarbonyl-1-adamanthyl amine, An N-t-butoxycarbonyl-N-methyl-1-adamanthyl amine, An N and N-G t-butoxycarbonyl-1-adamanthyl amine,

N, an N-G t-butoxycarbonyl-N-methyl-1-adamanthyl amine, N-t-butoxycarbonyl-4, 4'-diamino diphenylmethane, -G t-butoxy KARUBONIRUHEKISA methylene diamine, N and N, and N and N'N'-tetra-t-butoxy KARUBONIRUHEKISA methylene diamine, N and N'-G t-butoxycarbonyl-1, 7-diamino heptane, N and N'-G t-butoxycarbonyl-1, 8-diamino octane, N and N'-G t-butoxycarbonyl-1, 9-diamino nonane, N and N'-G t-butoxycarbonyl-1, 10-diamino decane, N and N'-G t-butoxycarbonyl-1, 12-diamino dodecane, N, N'-G t-butoxycarbonyl-4, 4'-diamino diphenylmethane, A N-t-butoxy cull BONIRUBENZU imidazole, N-t-butoxycarbonyl-2-methylbenzimidazol, Others [amino compounds /, such as N-t-butoxycarbonyl-2-phenyl benzimidazole / N-t-butoxycarbonyl group content], A formamide, N-methyl formamide, N,N-dimethylformamide, an acetamide, N-methyl acetamide, N,N-dimethylacetamide, a propione amide, a benzamide, a pyrrolidone, N-methyl pyrrolidone, etc. can be mentioned.

[0055] As said urea compound, urea, methyl urea, 1, and 1-dimethylurea, 1, 3-dimethylurea, 1, 1 and 3, 3-tetramethyl urea, 1, 3-diphenyl urea, tree n-butyl thiourea, etc. can be mentioned, for example. As said nitrogen-containing heterocyclic compound, for example An imidazole, 4-methyl imidazole, 4-methyl-2-phenylimidazole, benzimidazole 2-phenyl benzimidazole Imidazole derivatives, such as N-t-butoxycarbonyl-2-phenyl benzimidazole; A pyridine, 2-methylpyridine, 4-methylpyridine, 2-ethylpyridine, 4-ethyl pyridine, 2-phenyl pyridine, 4-phenyl pyridine, a 2-methyl-4-phenyl pyridine, Nicotine, a nicotinic acid, nicotinamide, a quinoline, 4-hydroxyquinoline, Pyridines, such as 8-oxyquinoline and an acridine; Others [piperazines /, such as a piperazine and 1-(2-hydroxyethyl) piperazine,], Pyrazine, a pyrazole, pyridazine, kino ZARIN, a pudding, a pyrrolidine, A piperidine, 3-piperidino-1, 2-propanediol, a morpholine, 4-methyl morpholine, 1, 4-dimethyl piperazine, 1, 4-diazabicyclo [2.2.2] An octane etc. can be mentioned.

[0056] Nitrogen-containing compound (b), an amide group content compound, a nitrogen-containing heterocyclic compound, etc. are desirable among these nitrogen-containing organic compounds. Said acid diffusion control agent is independent, or can mix and use two or more sorts.

[0057] Moreover, the alicycle group additive which has said acid dissociation nature machine is a component which shows the operation which improves further an adhesive property with dry etching resistance, a pattern configuration, and a substrate etc. As such an alicycle group additive, for example 1-adamantane carboxylic-acid t-butyl, 1-adamantane carboxylic-acid t-butoxy carbonylmethyl, 1, 3-adamantane dicarboxylic acid G t-butyl, 1-adamantane acetic-acid t-butyl, 1-adamantane acetic-acid t-butoxy carbonylmethyl, Adamantane derivatives, such as 1 and 3-ADAMANTANJI acetic-acid G t-butyl; Deoxycholic acid t-butyl, Deoxycholic acid t-butoxy carbonylmethyl, deoxycholic acid 2-ethoxyethyl, Deoxycholic acid 2-cyclohexyloxy ethyl, deoxycholic acid 3-oxocyclohexyl, Deoxycholate, such as deoxycholic acid tetrahydropyranyl and deoxycholic acid mevalonolactone ester; Lithocholic acid t-butyl, Lithocholic acid t-butoxy carbonylmethyl, lithocholic acid 2-ethoxyethyl, Lithocholic acid ester, such as lithocholic acid 2-cyclohexyloxy ethyl, lithocholic acid 3-oxocyclohexyl, lithocholic acid tetrahydropyranyl, and lithocholic acid mevalonolactone ester, can be mentioned. These alicycle group additives are independent, or two or more sorts can be mixed and used for them.

[0058] Moreover, said surfactant is a component which shows the operation which improves spreading nature, striae SHON, development nature, etc. As such a surface active agent, for example The polyoxyethylene lauryl ether, Polyoxyethylene stearylether, the polyoxyethylene oleyl ether,

Polyoxyethylene n-octyl phenyl ether, the polyoxyethylene n-nonylphenyl ether, By the following trade name besides the Nonion system surfactants, such as a polyethylene-glycol JIRAU rate and polyethylene-glycol distearate KP341 (Shin-Etsu Chemical Co., Ltd. make) and poly flow No.75 --- said --- No.95 (product made from Kyoeisha Chemistry) --- EFUTOPPU EF301, said EF303, said EF352 (product made from TOKEMU Products), the megger facsimile F171 --- said --- F173 (Dainippon Ink & Chemicals, Inc. make) --- Fluorad FC430, said FC431 (Sumitomo 3M make), the Asahi guard AG710 and Sir chlorofluocarbon S-382 --- said --- SC-101 --- said --- SC-102 --- said --- SC-103 --- said --- SC-104 --- said --- SC-105 --- said --- SC-106 (Asahi Glass Co., Ltd. make) etc. can be mentioned. These surfactants are independent, or two or more sorts can be mixed and used for them.

[0059] Moreover, said sensitizer absorbs the energy of a radiation, transmits the energy to an acid generator (B), shows the operation which increases the amount of generation of an acid by that cause, and has the effectiveness of raising the sensibility over which only a radiation-sensitive resin constituent is covered. As such a sensitizer, acetophenones, benzophenones, naphthalene, a biacetyl, eosine, a rose bengal, pyrenes, anthracene, and phenothiazins can be mentioned. These sensitizers are independent, or two or more sorts can be mixed and used for them. Moreover, by blending a color or a pigment, the latent image of the exposure section can be made to be able to visualize, the effect of the halation at the time of exposure can be eased, and an adhesive property with a substrate can be improved by blending an adhesion assistant. Furthermore, as an additive except said, the alkali fusibility resin mentioned later, the low-molecular alkali solubility control agent which has the protective group of acid dissociation nature, an antihalation agent, a preservation stabilizing agent, a defoaming agent, etc. can be mentioned.

[0060] (C) The solvent (henceforth "a solvent (C1)") which contains at least one sort chosen from the group of propylene-glycol-monomethyl-ether acetate, 2-heptanone, and a cyclohexanone as a (C) component in component this invention is desirable.

[0061] a solvent (C1) can contain solvents other than propylene-glycol-monomethyl-ether acetate, 2-heptanone, and a cyclohexanone (the following --- " --- others --- it is called solvent".) further. As other solvents, for example Propylene glycol monoethyl ether acetate, Propylene glycol mono---n-propyl ether acetate, propylene glycol mono---i-propyl ether acetate, Propylene glycol mono---n-butyl ether acetate, propylene glycol mono---i-butyl ether acetate, Propylene glycol monoalkyl ether acetate, such as propylene glycol mono---sec-butyl ether acetate and propylene glycol mono---t-butyl ether acetate; 2-butanone, 2-pentanone, 3-methyl-2-butanone, 2-hexanone, 4-methyl-2-pentanone, The ketones of the shape of a straight chain, such as 3-methyl-2-pentanone, 3, and 3-dimethyl-2-butanone and 2-octanone, and the letter of branching; Cyclopentanone, 3-methyl cyclopentanone, 2-methylcyclohexanone, 2, 6-dimethyl cyclohexanone, Annular ketones, such as an isophorone; 2-hydroxy methyl propionate, 2-hydroxy ethyl propionate, 2-hydroxy propionic-acid n-propyl, 2-hydroxy propionic-acid i-propyl, 2-hydroxy propionic-acid n-butyl, 2-hydroxy propionic-acid i-butyl, 2-hydroxy propionic-acid sec-butyl, 2-hydroxy propionic-acid alkyls, such as 2-hydroxy propionic-acid t-butyl; 3-methoxy methyl propionate, [0062] besides 3-alkoxy propionic-acid alkyls, such as 3-methoxy ethyl propionate, 3-ethoxy methyl propionate, and 3-ethoxy ethyl propionate N-propyl alcohol, i-propyl alcohol, n-butyl alcohol, T-butyl alcohol, a cyclohexanol, ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, the ethylene glycol mono---n-propyl ether, Ethylene glycol mono---n-butyl ether, diethylene-glycol wood ether, Diethylene-glycol diethylether,

diethylene glycol-di-n-propyl ether, Diethylene glycol-di-n-butyl ether, ethylene glycol monomethyl ether acetate, Ethylene glycol monoethyl ether acetate, ethylene glycol mono--n-propyl ether acetate, Propylene glycol monomethyl ether, the propylene glycol monoethyl ether, The propylene glycol mono--n-propyl ether, toluene, a xylene, 2-hydroxy-2-methyl ethyl propionate, ethoxy ethyl acetate, Hydroxyacetic acid ethyl, 2-hydroxy-3-methyl methyl butyrate, 3-methoxy butyl acetate, 3-methyl-3-methoxy butyl acetate, 3-methyl-3-methoxy butyl propionate, 3-methyl-3-methoxybutyl butyrate, ethyl acetate, n-propyl acetate, N-butyl acetate, methyl acetoacetate, an ethyl acetoacetate, methyl pyruvate, Pyruvic-acid ethyl, N-methyl pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, benzyl ethyl ether, di-n-hexyl ether, The diethylene-glycol monomethyl ether, diethylene glycol monoethyl ether, A caproic acid, a caprylic acid, 1-octanol, 1-nonanol, benzyl alcohol, benzyl acetate, ethyl benzoate, oxalic acid diethyl, a diethyl maleate, gamma-butyrolactone, ethylene carbonate, propylene carbonate, etc. can be mentioned.

[0063] The ketones of the shape of a straight chain and the letter of branching, annular ketones, propylene glycol monoalkyl ether acetate, 2-hydroxy propionic-acid alkyls, and 3-alkoxy propionic-acid alkyls are desirable among other solvents of these. A solvent besides the above is independent, or two or more sorts can be mixed and used for it.

[0064] the time of a solvent (C1) containing other solvents — the operating rate of other solvents — all solvents — receiving — usually — it is 70 or less % of the weight still more preferably 75 or less % of the weight preferably 85 or less % of the weight. Moreover, the total—solids concentration in a constituent of the amount of the (C) solvent used in the radiation-sensitive resin constituent of this invention is usually the amount which becomes 10 – 20 % of the weight still more preferably ten to 25% of the weight preferably five to 50% of the weight. After the radiation-sensitive resin constituent of this invention dissolves resin (A), an acid generator (B), and an additive component in the (C) solvent and uses them as a homogeneity solution, it is preferably used with the filter of about 0.2 micrometers of apertures, filtering.

[0065] Especially the radiation-sensitive resin constituent of formation approach this invention of a resist pattern is useful as a chemistry magnification mold resist. In said chemistry magnification mold resist, according to an operation of the acid generated from the acid generator by exposure, the acid dissociation nature machine in resin (A) dissociates, and a carboxyl group is produced, consequently the solubility over the alkali developer of the exposure section of a resist becomes high, and this exposure section is dissolved by the alkali developer, it is removed, and the resist pattern of a positive type is obtained. In case a resist pattern is formed from the radiation-sensitive resin constituent of this invention, after forming a resist coat and heat-treating beforehand by the case by applying a constituent solution on substrates, such as a silicon wafer and a wafer covered with aluminum, with proper spreading means, such as revolution spreading, flow casting spreading, and roll coating, (henceforth "PB"), it exposes on this resist coat so that a predetermined resist pattern may be formed. Although a visible ray, ultraviolet rays, far ultraviolet rays, an X-ray, a charged-particle line, etc. are used as a radiation used in that case according to the class of acid generator used, selecting suitably, the far ultraviolet rays represented with an ArF excimer laser (wavelength of 193nm) or a KrF excimer laser (wavelength of 248nm) are desirable, and especially an ArF excimer laser (wavelength of 193nm) is desirable. In this invention, heat-treating after exposure (henceforth "PEB") is desirable. By this PEB, the dissociative reaction of the acid dissociation nature machine in resin (A) advances smoothly. Although the heating conditions of PEB change with the combination presentation of a

radiation-sensitive resin constituent, they are usually 50–170 degrees C preferably 30–200 degrees C.

[0066] In order to pull out the potentia of a radiation-sensitive resin constituent in this invention to the maximum extent, For example, in order to prevent the effect of the basic impurity which can also form the antireflection film of an organic system or an inorganic system on the substrate used, and is contained in an environmental ambient atmosphere as indicated by JP,6-12452,B etc., For example, a protective coat can also be prepared on a resist coat, or these techniques can also be used together as indicated by JP,5-188598,A etc. Subsequently, a predetermined resist pattern is formed by developing the exposed resist coat. As a developer used for development, for example A sodium hydroxide, a potassium hydroxide, A sodium carbonate, silicic-acid sodium, meta-silicic-acid sodium, aqueous ammonia, Ethylamine, n propylamine, diethylamine, G n propylamine, Triethylamine, methyl diethylamine, ethyl dimethylamine, Triethanolamine, tetramethylammonium hydroxide, a pyrrole, The alkaline water solution which dissolved at least one sort of alkaline compounds, such as piperidine, choline, 1, 8-diazabicyclo-[5.4.0]-7-undecene, 1, and 5-diazabicyclo-[4.3.0]-5-nonene, is desirable. The concentration of said alkaline water solution is usually 10 or less % of the weight. In this case, if the concentration of an alkaline water solution exceeds 10 % of the weight, a non-exposed area is [a possibility of dissolving in a developer] and is not desirable, either.

[0067] Moreover, an organic solvent can also be added to the developer which consists of said alkaline water solution. As said organic solvent, for example An acetone, a methyl ethyl ketone, a methyl i-butyl ketone, Cyclopentanone, a cyclohexanone, 3-methyl cyclopentanone, Ketones, such as 2 and 6-dimethyl cyclohexanone; Methyl alcohol, Ethyl alcohol, n-propyl alcohol, i-propyl alcohol, n-butyl alcohol, t-butyl alcohol, cyclopentanol, Alcohols, such as cyclohexanol, 1, 4-hexandiol, 1, and 4-hexane dimethyol; A tetrahydrofuran, Ether, such as dioxane; aromatic hydrocarbon, such as ester; toluene, such as ethyl acetate, n-butyl acetate, and acetic-acid i-amyl, and a xylene, a phenol, acetonylacetone, dimethylformamide, etc. can be mentioned. These organic solvents are independent, or two or more sorts can be mixed and used for them. Below 100 capacity % of the amount of the organic solvent used is desirable to an alkaline water solution. In this case, when the amount of the organic solvent used exceeds 100 capacity %, development nature falls and there is a possibility that the development remainder of the exposure section may increase. Moreover, optimum dose addition of the surfactant etc. can also be carried out at the developer which consists of an alkaline water solution. In addition, after developing negatives with the developer which consists of an alkaline water solution, generally it washes with water and dries.

[0068]

[Embodiment of the Invention] Hereafter, an example is given and the gestalt of operation of this invention is explained still more concretely. However, this invention is not restrained at all by these examples. Here, the section is weight criteria unless it mentions specially. Each measurement and assessment in an example and the example of a comparison were performed in the following way.

Mw: It measured using the GPC column (two G2000HXL(s), one G3000HXL, and one G4000HXL) by TOSOH CORP. with the gel permeation chromatography (GPC) which makes mono dispersion polystyrene a criterion on analysis conditions with a flow rate tetrahydrofuran [a part for /and the elution solvent tetrahydrofuran of 1.0ml], and a column temperature of 40 degrees C.

The rate of a radioparency: The constituent solution was applied with the spin coat on quartz glass, and about the resist coat of 0.34 micrometers of thickness which formed by performing for [PB] 60 seconds on

the hot plate held at 90 degrees C, from the absorbance in the wavelength of 193nm, the rate of a radioparency was computed and it considered as the scale of the transparency in an far-ultraviolet-rays field.

[0069] Sensibility : The silicone wafer (ARC25) in which ARC25 (product made from Bruwer Science (Brewer Science)) film of 820A of thickness was formed on the front face is used as a substrate. A class product solution is applied with a spin coat on a substrate. On a hot plate On the resist coat of 0.34 micrometers of thickness which formed by performing PB on the conditions shown in a table 2, it exposed through the mask pattern with the ArF excimer laser aligner (the lens numerical aperture 0.55, exposure wavelength of 193nm) by NIKON CORP. Then, after performing PEB on the conditions shown in a table 2, with 2.38% of the weight of the tetramethylammonium hydroxide water solution, at 25 degrees C, negatives were developed for 60 seconds, and it rinsed, it dried, and the resist pattern of a positive type was formed. At this time, light exposure which forms line – and – tooth–space pattern (1L1S) with a line breadth of 0.16 micrometers in the line breadth of 1 to 1 was made into the optimal light exposure, and this optimal light exposure was made into sensibility.

Resolution: The dimension of the minimum resist pattern resolved with the optimal light exposure was made into resolution.

[0070] Dry–etching resistance: It is a dry etching system (Pinnacle8000) by the PMT company to the resist coat of 0.5 micrometers of thickness which applied the constituent solution with the spin coat, and dried and formed it on the silicone wafer. It uses and is CF4 about etching gas. It carried out, dry etching was performed on condition that quantity–of–gas–flow 75sccm, pressure 2.5mTorr, and output 2,500W, the etch rate was measured, and the relative value to the etch rate of the coat which consists of cresol novolak resin estimated the relative etch rate. It means excelling in dry etching resistance, so that an etch rate is small. Pattern configuration: Line – and the lower side dimension Lb of the rectangle–like cross section of – tooth–space pattern (1L1S) with a line breadth of 0.16 micrometers Top chord dimension La The pattern configuration made “good” the case where measured with a scanning electron microscope, and satisfied $0.85 \leq La/Lb \leq 1$, and the pattern configuration was not lengthening the skirt.

[0071] Synthetic example 12–methyl–2–adamantyl methacrylate 50.55g (50–mol %), 3–hydroxy–1–adamantyl methacrylate 25.49g (25–mol %), and R3 The monomer solution which dissolved in 2–butanone 200g and used as the homogeneity solution 23.97g [of methacrylic ester which gives the repeat unit (1–3) which is a methyl group] (henceforth “methacrylic ester (alpha)”) (25–mol %), and azobisiso valeric–acid methyl 3.97g was prepared. Moreover, after carrying out the nitrogen purge of the 1000ml three necked flask which supplied that [2–butanone 100g] for 30 minutes, it heated at 80 degrees C, stirring the inside of a flask, and said monomer solution was dropped at the rate for 10ml / 5 minutes using the tap funnel. The polymerization was carried out by considering the time of dropping initiation as a polymerization initiation event for 5 hours. The reaction solution was cooled at 30 degrees C or less after polymerization termination, it supplied into methanol 2,000g and the depositing white powder was carried out the ** exception. Then, white powder was mixed with methanol 400g, after repeating twice the actuation which makes a slurry and is stirred and washing it, it carried out the furnace exception, it dried at 50 degrees C for 17 hours, and the resin (73g, 73 % of the weight of yield) of white powder was obtained. The content of each repeat unit to which Mw is 10,000 and originates in 2–methyl–2–adamantyl methacrylate,

3-hydroxy-1-adamanthyl methacrylate, and methacrylic ester (alpha) of this resin was the copolymer of 45.3:25.1:29.6 (mol %). Let this resin be resin (A-1).

[0072] Synthetic example 22-methyl-2-adamanthyl methacrylate 50.85g (50-mol %), 3-hydroxy-1-adamanthyl methacrylate 15.39g (15-mol %), The resin (71g, 71 % of the weight of yield) of white powder was obtained like the synthetic example 1 except having used the monomer solution which dissolved in 2-butanone 200g and used 33.76g [of methacrylic ester] (alpha) (35-mol %), and azobisiso valeric-acid methyl 4.00g as the homogeneity solution. The content of each repeat unit to which Mw is 10,500 and originates in 2-methyl-2-adamanthyl methacrylate, 3-hydroxy-1-adamanthyl methacrylate, and methacrylic ester (alpha) of this resin was the copolymer of 46.2:15.6:38.2 (mol %). Let this resin be resin (A-2).

[0073] Synthetic example 32-methyl-2-adamanthyl methacrylate 51.01g (50-mol %), 3-hydroxy-1-adamanthyl methacrylate 10.29g (ten-mol %), The resin of white powder was obtained like the synthetic example 1 except having used the monomer solution which dissolved in 2-butanone 200g and used 38.70g [of methacrylic ester] (alpha) (40-mol %), and azobisiso valeric-acid methyl 4.01g as the homogeneity solution (75g, 75 % of the weight of yield). The content of each repeat unit to which Mw is 11,200 and originates in 2-methyl-2-adamanthyl methacrylate, 3-hydroxy-1-adamanthyl methacrylate, and methacrylic ester (alpha) of this resin was the copolymer of 45.6:9.8:44.6 (mol %). Let this resin be resin (A-3).

[0074] Synthetic example 42-methyl-2-adamanthyl methacrylate 45.89g (45-mol %), 3-hydroxy-1-adamanthyl methacrylate 15.43g (15-mol %), The resin of white powder was obtained like the synthetic example 1 except having used the monomer solution which dissolved in 2-butanone 200g and used 38.69g [of methacrylic ester] (alpha) (40-mol %), and azobisiso valeric-acid methyl 4.01g as the homogeneity solution (72g, 72% of yield). The content of each repeat unit to which Mw is 10,200 and originates in 2-methyl-2-adamanthyl methacrylate, 3-hydroxy-1-adamanthyl methacrylate, and methacrylic ester (alpha) of this resin was the copolymer of 40.2:15.3:44.5 (mol %). Let this resin be resin (A-4).

[0075]

[Example] Various assessment was performed about the class product which consists of a component shown in examples 1-6 and example of comparison 1 table 1. An assessment result is shown in a table 3. Components other than resin (A-1) – (A-5) in a table 1 are as follows.

Other resin a-1: T-butyl methacrylate / methyl methacrylate / methacrylic-acid copolymer (copolymerization mole-ratio =40/40/20, Mw=20,000)

[0076] Acid generator (B)

B-1: 1- Tetrahydro thio FENIUMUNONA fluoro-n-butane sulfonate B-2:1-(4-n-butoxy naphthalene-1-IRU) tetrahydro thio FENIUMU perfluoro-n-octane sulfonate B-3:1- (4-n-butoxy naphthalene-1-IRU)

Tetrahydro thio FENIUMUNONA fluoro-n-butane sulfonate B-4:1-(3, 5-dimethyl-4-hydroxyphenyl) tetrahydro thio FENIUMU perfluoro-n-octane sulfonate B-5 : (3, 5-dimethyl-4-hydroxyphenyl)

Triphenylsulfonium nona fluoro-n-butane sulfonate [0077] an acid diffusion control agent --

D-1:N-t-butoxycarbonyl-2-phenyl benzimidazole D-2: -- the N-t-butoxy cull BONIRUJI cyclohexylamine

D-3:2-phenyl benzimidazole [0078] (C) solvent C-1:propylene-glycol-monomethyl-ether acetate C-

2:2-heptanone C-3:cyclohexanone gamma-1: -- gamma-butyrolactone [0079]

[A table 1]

表 1

	樹脂 (g)	酸発生剤 (B) (g)	酸放出抑制剤 (g)	溶剤 (g)
実施例1	A-1 (100)	B-3 (5)	D-3 (0.11)	C-2 (600)
実施例2	A-1 (100)	B-3 (4) B-5 (1)	D-3 (0.24)	C-2 (600)
実施例3	A-1 (100)	B-1 (4) B-5 (1)	D-3 (0.45)	C-2 (450) C-3 (200)
実施例4	A-2 (100)	B-2 (4) B-5 (1)	D-3 (0.45)	C-1 (550) γ-1 (50)
実施例5	A-3 (100)	B-4 (5)	D-3 (0.11)	C-2 (600)
実施例6	A-4 (100)	B-3 (4) B-5 (1)	D-3 (0.24)	C-3 (600)
比較例1	a-1 (100)	B-5 (3)	D-1 (0.60)	C-3 (600)

[0080]

[A table 2]

表 2

	レジスト被膜 の膜厚 (μm)	基板の種類	P B		P E B	
			温度 (°C)	時間 (秒)	温度 (°C)	時間 (秒)
実施例1	0.34	ARC25	130	90	130	90
実施例2	0.34	ARC25	130	90	130	90
実施例3	0.34	ARC25	130	90	130	90
実施例4	0.34	ARC25	125	90	125	90
実施例5	0.34	ARC25	130	90	125	90
実施例6	0.34	ARC25	130	90	130	90
比較例1	0.34	ARC25	130	90	130	90

[0081]

[A table 3]

表 3

	放射線透過率 (193nm, %)	感度 (J/m ²)	解像度 (μm)	ドライエッティング 耐性	パターン形状
実施例1	72	153	0.13	0.6	良好
実施例2	75	161	0.14	0.7	良好
実施例3	71	169	0.13	0.6	良好
実施例4	76	172	0.14	0.6	良好
実施例5	73	151	0.13	0.7	良好
実施例6	74	172	0.13	0.6	良好
比較例1	67	192	0.18	1.0	良好

[0082]

[Effect of the Invention] The radiation-sensitive resin constituent of this invention as a chemistry magnification mold resist which induces the far ultraviolet rays represented by an activity beam of light (wavelength of 248nm), for example, a KrF excimer laser, or the ArF excimer laser (wavelength of 193nm). While the transparency especially over a radiation is high, and being high resolution and excelling in sensibility, dry etching resistance, a pattern configuration, etc. By combining resin, a specific acid generator, and a specific solvent, the adhesive property over a substrate and the skirt configuration of a pattern also become good, and can be used very suitable for manufacture of the integrated circuit device expected that detailed-ization will advance increasingly from now on.

[Translation done.]